

Article

Electronic Structure of Intermetallic Antiferromagnet GdNiGe

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Abstract: The electronic structure of the GdNiGe ternary intermetallic compound was investigated in this work. We carried out the spin-polarized DFT+U calculations of its band structure within generalized gradient approximation accounting for strong electronic correlations in the 4f-shell of gadolinium ions. The antiferromagnetic ordering was reproduced in the calculations, in agreement with experimental data. The calculated equilibrium volume is within 2% accuracy to the experimental crystal structure data, which demonstrates the reliability of the method chosen. The 4f-shell of Gd was demonstrated to substantially contribute to the spectral and magnetic properties of the GdNiGe compounds, whereas other ions were found nonmagnetic, in agreement with experimental data.

Keywords: electronic structure; DFT+U; intermetallic compound; antiferromagnetic ordering

1. Introduction

Increased interest in the study of intermetallic compounds of the RTX family (where R is a rare-earth metal, T and X are d- and p-elements, respectively) appeared in the process of targeted search and obtaining new compounds with functionally significant properties. With a wide variety of physical characteristics, compounds of this series possess a number of unique qualities, the use of which is considered promising for practical use—see the review [1] and references therein. Such properties include, for example, giant magnetocaloric [2] and magnetoresistive [3] effects, on the basis of which it is possible to create a magnetic refrigerator and sensor devices. It has been established that large magnitudes of these effects are observed in ternary compounds with Gd and heavy rare-earth metals and are caused by changes in the magnetic state of constituent metal ions when an external magnetic field is applied. The anomalies occurring are accompanied by a change in the electronic structure, magnetic moments, and transport properties. For this reason, the understanding of these properties is required to understand further functional properties of these compounds for their possible use.

For GdNiGe, experimental studies of magnetic properties in the temperature range 4.2–300 K and in magnetic fields up to 20 kOe were carried out in [4]. In [5], electrical resistivity, thermopower, and thermal conductivity studies in GdNiGe revealed the peaks in these characteristics near the ordering temperature. In [6], the heat capacity was studied in the temperature range from 2 to 40 K, and the change of the magnetic entropy was obtained for GdNiGe from the temperature dependence of the magnetic heat capacity. The GdNiGe intermetallic compound was shown to be antiferromagnetically ordered with a Néel temperature of $T_N = 10.7$ [6], 11 [5] K, and the reciprocal susceptibility above 60 K following the Curie–Weiss law [4]. Further studies of magnetic ordering, spectral, and electronic properties of GdNiGe are completely missing in the literature. This work is aimed at studying the electronic structure and magnetic properties of the GdNiGe intermetallic

compound based on theoretical ab initio approach, accounting for electronic correlations in the Gd ions that were not reported earlier.

2. Computational Method

The electronic structure was calculated using the DFT+U method [7] in the Quantum ESPRESSO software package [8,9] using the exchange-correlation potential in the approximation of the generalized gradient correction (GGA) version of Perdew–Burke–Ernzerhof (PBE) [10]. The wave functions were decomposed over plane waves, and the interactions between ions and valence electrons were taken into account in the framework of the method of associated plane waves (PAW). In the calculations, the PAW potentials Gd.GGA-PBE-paw-v1.0.UPF [11], Ni.pbe-n-kjpaw_psl.0.1.UPF and Ge.pbe-dn-kjpaw_psl.0.2.2.UPF were obtained from the ATOMPAW program [12]. To obtain sufficient convergence in the self-consistency cycle, the calculation used the energy cutoff for plane waves, equal to 60 Ry. The integration in the reciprocal space was performed on a grid of $8 \times 8 \times 8$ k -points. To take into account the strong electron correlations of the 4f-electrons of Gd, the U correction was included for the parameters of the direct Coulomb $U = 6.7$ eV and Hund exchange $J = 0.7$ eV interactions. These values were previously calculated and used for gadolinium in [7,13].

3. Crystal Structure

The GdNiGe compound crystallizes in the hexagonal TiNiSi-type Pnma structure (space group 62) with 4 formula units (12 atoms) in the unit cell with lattice parameters $a = 4.310$ Å, $b = 6.935$ Å, and $c = 7.315$ Å [4]. The atomic positions are presented in Table 1. Gadolinium ions occupy 4c positions (0.0212, 0.25, 0.6803), nickel ions are also in 4c positions (0.142, 0.25, 0.0609), and germanium ions are in 4c positions with the coordinates (0.2651, 0.25, 0.3771) [4]. In the calculations, we used the experimental values of the atomic positions and obtained the calculated equilibrium volume with the fixed c/a ratio and all angles in GdNiGe. The crystal structure of GdNiGe is shown in Figure 1.

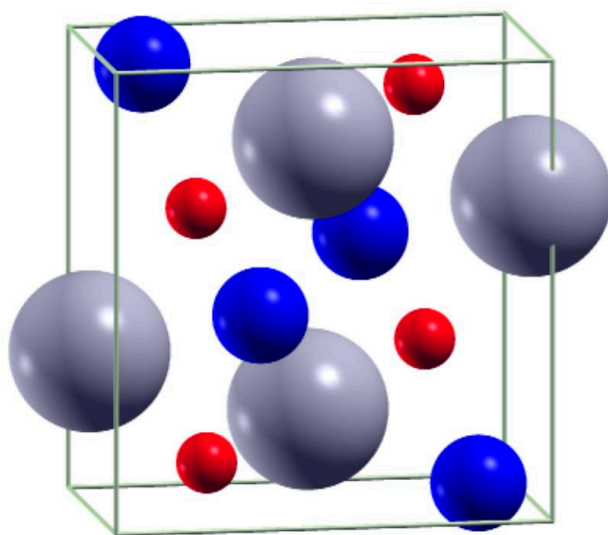


Figure 1. The crystal structure of the GdNiGe intermetallic compound. Grey spheres represent Gd, red—Ge and blue ones—Ni.

Table 1. Atomic coordinates in the compound GdNiGe [4].

Ion	Point Symmetry	x	y	z
Gd	4c	0.0212	0.25	0.6803
Ni	4c	0.142	0.25	0.0609
Ge	4c	0.2651	0.25	0.3771

4. Results

When performing the DFT+U calculations, an antiferromagnetic ordering of the magnetic moments of gadolinium ions was simulated in accordance with experimental data [6]. As expected, the nickel and germanium ions in the self-consistency circle of the calculations remained nonmagnetic with magnetic moments of maximum up to $0.02 \mu_B$, which manifested itself in unpolarized partial densities of the electronic states for these ions. In [14], it was concluded that Ni is nonmagnetic in RNiGe series compounds. The following Lowdin charges were obtained in the calculations for Gd: 2.18 (s), 5.88 (p), 2.49 (d), 7.23 (f); for Ni: 0.48 (s), 1.31 (p), 8.60 (d); for Ge: 1.12 (s), 2.67 (p). As a result of the self-consistent calculations, the total magnetic moment of $7.35 \mu_B$ per formula unit of GdNiGe was calculated, which slightly underestimated (about 6%) the experimental value of $7.85 \mu_B$ [4]. Further experimental studies are required to check possible reasons for this mismatch, including X-ray diffraction, Rietveld refinement data, and neutron and magnetic measurements. The magnetic moments of the Gd ion are altered antiferromagnetically for the nearest Gd ions in the c-direction, while being coupled ferromagnetically in a slab-like structure with the close z coordinates of the Gd ions.

In Figure 2, the volume dependence of the total energy for GdNiGe is shown. It is clear that the DFT+U calculated equilibrium volume for GdNiGe (1498 a.u.^3) is in a very good agreement with the experimental value (1475.4863 a.u.^3), with a deviation of less than 2%. This agreement confirms the correctness of the theoretical method DFT+U and corresponding parameters chosen in this work to investigate the electronic structure of the GdNiGe compound.

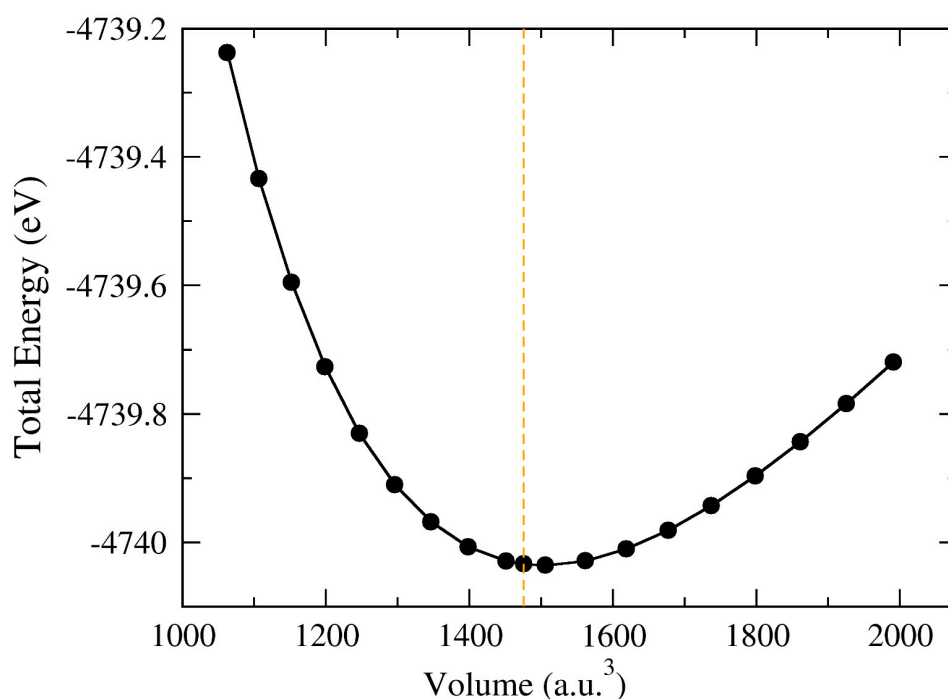


Figure 2. The volume dependence of the total energy for GdNiGe. The dashed line shows the experimental volume [4].

Figure 3 shows the density of states (DOS) based on one formula unit of the GdNiGe intermetallic compound for two opposite spin directions, i.e., spin up and down. The Fermi level passes through zero energy. The density of states in the GdNiGe compound for two opposite projections of spin is the same, since the resulting state is antiferromagnetically ordered. The two intense peaks in the GdNiGe compound are formed by the localized electronic states of the Gd 4f-character centered near -7.3 eV in the occupied part and near 4.8 eV in the empty electronic states—see Figure 3a. These two peaks correspond to the half-filled 4f-shell of gadolinium.

These electronic states of gadolinium are very localized, which is clearly seen in Figure 4, showing the band structure of GdNiGe from our DFT+U calculations. In these very similar spin projections Figure 4a,b, these localized 4f-states are manifested as the tight bunches of bands at the corresponding energies. The other bands are highly dispersive and mixed in almost all energy intervals. In this energy range, the concentration of the bands is higher because of the Ni-3d states in the -2 to -1 eV energy interval. In agreement with the DOS Figure 3, the Fermi energy in band structure is crossed by a number of bands, confirming the metallic state of GdNiGe.

Because of the antiferromagnetic ordering and spin polarization, the Gd magnetic moments in Figure 3b for the first type of the Gd ions (Gd₁ and Gd₂) and the second type of the Gd ions (Gd₃ and Gd₄) are in the opposite spin direction in the occupied and empty energy parts. Because the nickel and germanium ions are found to be nonmagnetic, it manifested itself in the unpolarized partial densities of the electronic states for these ions. The largest contribution from these ions comes from the 3d states of nickel in the energy range from -5 eV to 1 eV above the Fermi level, and partially, the 4p germanium states from -5 eV to 1 eV, and smoothly in the higher energies. These states together with the 5d and other Gd states form the metallic character of the GdNiGe compounds, providing the electronic states at the Fermi energy.

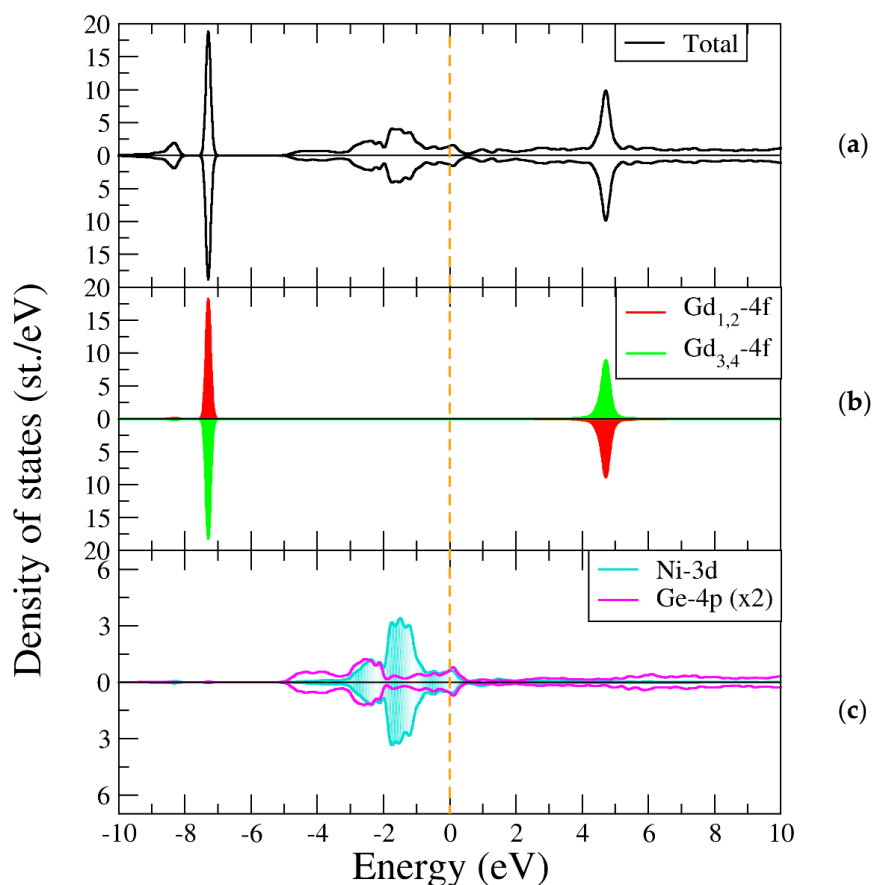


Figure 3. The density of states of GdNiGe from DFT+U. (a) Total density of states per f.u.; (b) partial density of states for Gd-4f; (c) partial density of states for Ni-3d and Ge-4p ($\times 2$). The Fermi energy is shown as a dashed line.

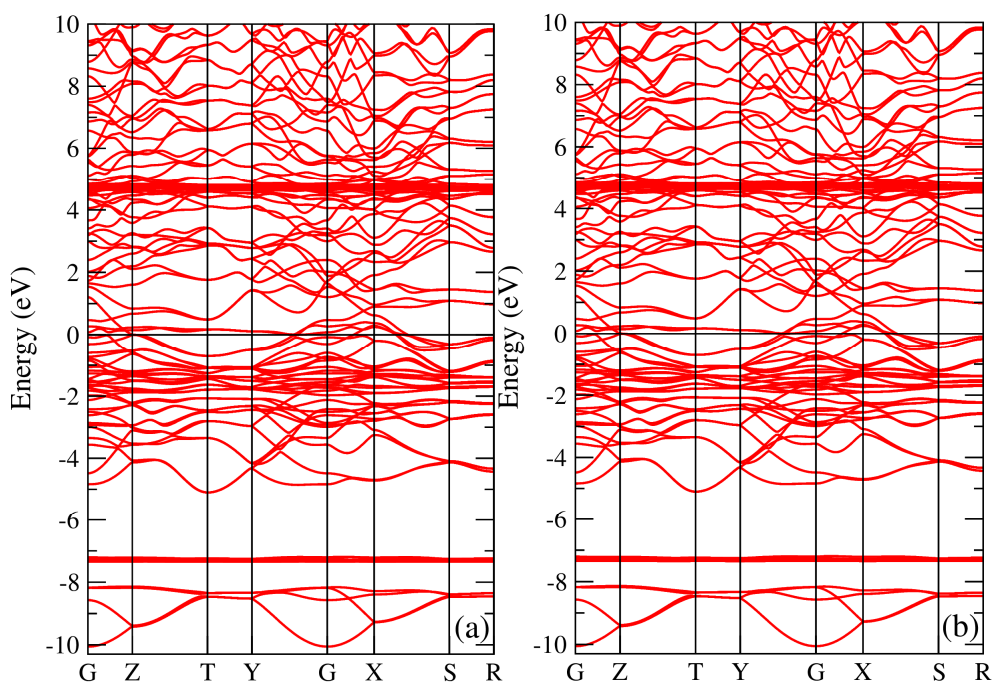


Figure 4. Band structure of GdNiGe from DFT+U. (a) For the spin up projection; (b) for the spin down projection. The Fermi energy is shown as a line at zero energy.

5. Conclusions

The electronic and band structure, as well as magnetic properties of the ternary intermetallic compound GdNiGe from the RNiGe series were calculated using the DFT+U calculations based on both generalized gradient approximation and accounting for strong electronic correlations in the 4f-shell of Gd. The antiferromagnetic ordering of Gd ions and nonmagnetic characteristics of Ni and Ge ions were reproduced in the calculations. The calculated equilibrium volume of GdNiGe is within 2% accuracy to the experimental value, which demonstrates the reliability of the DFT+U method for this intermetallic compound. The 4f-shell of Gd was found half-filled to substantially contribute to the spectral and magnetic properties of the GdNiGe compounds, whereas other ions were found nonmagnetic in agreement with experimental data.

Author Contributions: E.D.B. and A.V.L. carried out the theoretical calculations and prepared the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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